United States Patent Office

Patented Nov. 2, 1965

1

3,215,647 SYNTHETIC RUBBER LATEX FOAM CONTAINING A COREACTIVE MATERIAL AND PROCESS OF MAKING SAME

Edwin R. Dunn, Midland, Mich., assignor to The Dow Chemical Company, Midland, Mich., a corporation of Delaware

No Drawing. Filed June 19, 1962, Ser. No. 203,448 23 Claims. (Cl. 260—2.5)

This invention relates to making improved synthetic latex solid foams. More particularly, it relates (1) to an improved method for the preparation of synthetic latex solid foams comprising an improved gelation technique and simplified compounding which increases the range of composition and of solids concentration of emulsion polymers which are usable to make foamed products, (2) to the solid foam produced by such a method and (3) to articles coated by a solid foam prepared by such a method.

It is known to prepare foam rubber from a polymer in the form of an aqueous emulsion. Such a process comprises forming a foam structure by chemical blowing agents or by whipping or otherwise aerating the latex which has been compounded with antioxidants, accelerators and vulcanizing agents in the usual manner, together with frothing aids, such as soap solutions; after forming such foam, a cogulating or destabilizing agent, having a delayed action, such as sodium silicofluoride, is added; by suitable adjustments of the amount of coagulating agent and the temperature of the mixing step, the foam remains sufficiently stable that it may be introduced into molds, or spread on a flat tray or belt, or coated onto fabrics, then gelled and subsequently vulcanized, often in steam at atmospheric pressure. The cellular article may then be removed, washed and dried. In a somewhat different process, in which the foaming step occurs after the material is placed in a mold, hydrogen peroxide is added to the compounded latex along with a peroxide decomposition catalyst; the liquid composiiton then is placed in molds where a delayed decomposition of the peroxide occurs thus liberating oxygen which expands the material into a cellular structure that fills the mold; subsequent freezing maintains the expanded structure while a gas such as carbon dioxide permeates the structure and coagulates the material into the permanent structure; vulcanization and subsequent steps are carried out as in the previously described method.

The polymers which may be used in these prior art processes are limited almost exclusively to natural rubber, to certain polymers of 2-chloro-1,3-butadiene and to the GRS cold rubbers because of requirements for high solids concentration and early development of strength in wet coagulated foam in the most widely used processes, and/or by the requirements for polymers which are film forming at low temperatures in the processes which use freezing for the initial setting of the foam. Other disadvantages arise from the compounding difficulties of incorporating the vulcanizing agents, and related materials, 60 into the aqueous emulsion. A still further disadvantage arises from the discoloration and staining which occurs because of the presence of usual vulcanizing agents and related additives.

It is an object of this invention to provide new and advantageous means for making latex foam products. A more particular object is to provide a method for making latex foam products. A further object is to provide a process for making latex foam products which can be cured without the use of the usual sulfur-containing vulcanizing agents, or other vulcanizing agents acting in substantially the same manner, and without the usual acces-

2

sory vulcanizing ingredients. A still further object is to provide latex foam products with improved initial color and non-staining features, and better resistance to color change and deterioration of other desirable properties with age. Other objects will be apparent from the following description.

These objects have been accomplished by the discovery, and this discovery is the subject of this invention, that when a latex comprising a polymer having certain reactive substituent groups is intimately mixed with an aqueous or water-miscible solution or an aqueous dispersion of a coreactive material containing one or more carbon atoms and additionally which has at least two of certain substituent groups coreactive with the reactive groups on the latex polymer, and then the mixture is foamed by mechanical or chemical means, placed into molds or spread onto a suitable support or substrate, the foam gels to a stable foam structure at a rate which is controlled by adjustment of the composition and concentration of the reactants and of the temperature and pH of the system; the solid foam is then cured without the addition of the usual vulcanizing agents and accessory compounds; and the resulting products have good initial color, are nonstaining and have improved resistance to change in the desirable properties with age.

To prepare the latexes applicable to the practice of this invention at least two polymerizable, ethylenically unsaturated monomers, of the class of styrene and monomers copolymerizable with styrene, are copolymerized in an emulsion system to form a latex copolymer which is film forming below 250° F. or can be made film forming at that temperature by the addition of solvents or plasticizers.

At least one of such monomers which is copolymerized to form a latex for use in the instant invention consists of those polymerizable, ethylenically unsaturated monomers which have pendant reactive substituent groups such as carboxy, sulfo, primary amino, secondary amino, carboxamido, methylolcarboxamido, sulfonamido, primary hydroxyl, secondary hydroxyl, phenolic hydroxyl, aldehydic, and epoxy groups or which have substituent groups which, subsequent to polymerization, can be converted to such reactive substituent groups, e.g., ester, nitrile, amide, or salt groups which can be hydrolyzed to reactive acid, amine, or hydroxyl groups. Examples of such ethylenically unsaturated monomers having pendant reactive substituent groups are acrylic acid, methacrylic acid, itaconic acid, fumaric acid, maleic acid, ethyl acid maleate, 2-sulfoethyl acrylate, 2-sulfoethyl methacrylate, 2-aminoethyl methacrylate hydrochloride, 2-aminoethyl acrylate hydrochloride, vinyl benzylamine, glycidyl methacrylate, hydroxystyrene, acrolein, methacrolein, allyl alcohol, vinylbenzyl alcohol, 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, acrylamide, bis-N-methylol acrylamide, Nmethylolacrylamide, N-methylolmethacrylamide, bis-Nmethylolmethacrylamide, methacrylamide, $N-\beta$ -hydroxyethyl acrylamide, N- β -hydroxyethyl methacrylamide, β hydroxypropyl acrylate, β -hydroxypropylmethacrylate, $\gamma\text{-hydroxypropyl}$ acrylate, $\gamma\text{-hydroxypropyl}$ methacrylate, 6-hydroxyhexyl acrylate, 6-hydroxyhexyl methacrylate, sodium styrene sulfonate, sodium α-methylstyrene sulfonate, 2-methylaminoethyl acrylate hydrochloride, 2methylaminoethyl methacrylate hydrochloride, 3-methylaminopropyl acrylate hydrochloride, 3-methylaminopropyl methacrylate hydrochloride, 3-methylaminobutyl acrylate hydrochloride, 3-methylaminobutyl methacrylate hydrochloride, 3-ethylaminopropyl acrylate hydrochloride, and styrene sulfonamide.

Among the ethylenically unsaturated monomers of the class of styrene and monomers copolymerizable with styrene are the monomers having reactive substituent groups